

PATENT ABSTRACTS OF JAPAN

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(54) NON-AQUEOUS ELECTROLYTE CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a non-aqueous electrolyte cell having highly voltage, capacity, and energy density and which indicates highly charging/discharging cyclic characteristic, and is highly safe by constitution the main component of the negative active material of the covalent bond crystal of the prescribed electric conductivity.

SOLUTION: The concentration of impurities in a mixed manner is generally one donor atom or one acceptor atom for 10⁷-10⁶ silicon atoms, but preferably, doping with high concentration is suitable, and the concentration of one donor atom or one acceptor atom for 10⁴ silicon atoms or higher concentration is preferable. Electric conductivity σ to be obtained by doping these impurities is preferably $\geq 10^{-5} \text{Scm}^{-1}$ at 20°C, more preferably, $\geq 10^{-2} \text{Scm}^{-1}$ and most preferably $\geq 1 \text{Scm}^{-1}$. The covalent bond crystal is preferably a powder material, whose means grain size is 0.1-500 μm .

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CLAIMS

[Claim(s)]

[Claim 1] The nonaqueous electrolyte cell by which the quality of a main truss product of a negative-electrode active material is characterized by electrical conductivity sigma consisting of a covalent crystal beyond 10^{-5}Scm^{-1} at 20 degrees C.

[Claim 2] A nonaqueous electrolyte cell according to claim 1 with said powdered negative-electrode active material.

[Claim 3] The nonaqueous electrolyte cell according to claim 1 whose covalent crystal of said negative-electrode active material is a single crystal.

[Claim 4] The nonaqueous electrolyte cell according to claim 3 by which said single crystal consists of silicon.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the negative-electrode active material in more detail about a nonaqueous electrolyte cell.:

[0002]

[Description of the Prior Art] Although it was more typical than before as a negative-electrode active material for nonaqueous electrolyte cells to have used a lithium, there was a problem in respect of a cycle life for an arborescence deposit (dendrite) of the lithium generated at the time of charge. Moreover, this dendrite penetrates a separator, and an internal short circuit is caused or it causes ignition.

[0003] Moreover, the alloy with a metal lithium was also used in order to prevent the dendrite generated at the time of the above charge, but when the charge became large, there were problems, such as fine pulverization of a negative electrode and omission of a negative-electrode active material.

[0004] The cell which uses a carbon material for a negative electrode for current, reinforcement, and safety attracts attention, and is put in practical use in part. However, the carbon material used for a negative electrode had the problem that an internal short circuit and decline in charging efficiency arose, at the time of boosting charge. Generally, since the dope potential of the lithium to a carbon material was close to 0V, potential might become less than [0V] and these carbon materials might deposit the lithium on the electrode, when boosting charge was performed. Therefore, the internal short circuit of a cel is caused or it becomes the cause that discharge effectiveness falls. Moreover, although the improvement with such a carbon material remarkable in respect of a cycle life is made, since the consistency is comparatively small, the capacity per volume will become low. That is, this carbon material is still insufficient from the point of a high energy consistency. Moreover, initial charge-and-discharge effectiveness falls about what needs to form a coat on carbon, and since quantity of electricity used for this coat formation is irreversible, it leads to the capacity lowering for that quantity of electricity.

[0005] On the other hand, multiple oxide $\text{Li}_x \text{Si}_{1-y} \text{M}_y \text{O}_z$ (JP,7-230800,A) containing silicon and a lithium and using amorphous chalcogen compound $\text{M}_1 \text{M}_2 \text{p M}_4 \text{q}$ (JP,7-288123,A) are advocated as negative-electrode active materials other than a metal lithium, a lithium alloy, or a carbon material, and it is improved in respect of high capacity and a high energy consistency.

[0006] However, since the own electrical conductivity of an active material of the above multiple oxides was low, the problem was in boosting charge and a load characteristic. Although addition of an electric conduction agent is tried in order to solve this problem, in order to acquire the charge-and-discharge property that satisfaction is obtained, it is necessary to use amount sufficient as an electric conduction agent for a carbon material with a low consistency, and the capacity per volume will fall.

[0007] Moreover, since a multiple oxide etc. was considered that a reaction with a lithium advances through reduction of oxide since the ingredient itself is oxide, especially the irreversible reduction in the first stage might take place, and initial charge-and-discharge effectiveness might become low. Therefore, by the further high capacity and the high energy consistency, a cycle life is long and development of the safe negative-electrode ingredient for nonaqueous electrolyte cells is desired.

[0008]

[Problem(s) to be Solved by the Invention] That is, although it is advantageous in respect of high tension and safety when a problem has an advantage as high tension, and high capacity and a high energy consistency on the cycle nature of a certain thing, or safety when using the alloy of a lithium metal, or a lithium and a metal as a negative electrode, and using a carbon material, the field of high capacity and a high energy consistency is inadequate. Furthermore, when using an oxide negative electrode, the point of high capacity and a high energy consistency is not satisfactory in respect of high tension, a charge-and-discharge effectiveness property, and a cycle life or safety, although it seems that it is improved.

[0009] For this reason, in order to show the outstanding charge-and-discharge cycle property and to obtain a rechargeable battery with high safety by high tension and the high energy consistency, there are few change and the volume changes of crystal system in the case of occlusion bleedoff of the lithium at the time of charge and discharge, and it is expected the compound which is an operating space near lithium potential as much as possible, and has reversibly the conductivity which can occlusion emit a lithium.

[0010]

[Means for Solving the Problem] This invention is made in view of the above-mentioned trouble, and it is characterized by electrical conductivity sigma consisting [the quality of a main truss product of a negative-electrode active material] of a covalent crystal beyond 10^{-5}Scm^{-1} at 20 degrees C as an ideal negative-electrode active material used for a nonaqueous electrolyte cell.

[0011] Furthermore, as for the quality of a main truss product of the negative-electrode active material mentioned above, consisting of a powder-like silicon single crystal is desirable.

[0012] previously -- as the alloy of a lithium and silicon -- Binary Alloy Phase it is in Diagrams (p2465) -- as -- $\text{Li}_{22}\text{Si}_5$ up to -- alloying by presentation is known. Moreover, JP,5-74463,A has reported that a cycle property improves by using the single crystal of silicon for a negative electrode. However, when silicon was made to dope a lithium as negative-electrode material of the nonaqueous electrolyte cell for rapid charges and discharges and having been tried as like, it turned out that a lithium deposits without a dope hardly taking place. Then, as a result of this invention persons' performing examination on an electronic conduction disposition about a covalent crystal, it turned out that the occlusion of a lithium and bleedoff advance smoothly, without the phenomenon of a deposit of a lithium happening. Furthermore, it turned out that this reaction advances with the potential very near lithium potential about 0.1V, the high capacity near geometric capacity is obtained, and it excels in reversibility.

[0013] That is, although the alloy of a lithium and silicon was known, it was the intrinsic semiconductor of a covalent crystal originally, if silicon itself remained as it was, its electronic conduction nature was low, and the property as a cell negative-electrode ingredient was bad [itself]. Therefore, although it was the raw material which cannot be easily set as the object of research, it found out that electronic conduction nature improved and occlusion bleedoff of a lithium took place easily by doping the atom which can become silicon with a donor atom and an acceptor atom as an ingredient built into the interior of a cell. It turned out that phenomena, such as breaking or impalpable-powder-izing of a crystal, or omission, are not seen by using silicon as a single crystal especially, but a cycle property improves.

[0014]

[Embodiment of the Invention] Although the charge-and-discharge property which Si, germanium,

GaAs, GaP, InSb, GaP, SiC, BN, etc. were mentioned, among those was excellent about especially silicon as a covalent crystal said here is acquired, and it is abundant in resource, and it is desirable especially since toxicity is low, it is not limited to these. Moreover, although it is desirable since the charge-and-discharge property which a single crystal, polycrystal, and amorphous ** were mentioned about the crystal system, among those was excellent about especially the single crystal is acquired, it is not limited to these.

[0015] Furthermore, this covalent crystal can contain an impurity in order to raise electronic conduction nature. Although the impurity said here can serve as a donor atom and an acceptor atom among all the elements of the periodic table and are P, aluminum, As, Sb, B, Ga, In, etc. preferably, it is not limited to these.

[0016] as the approach of obtaining the single crystal of silicon -- a CZ process (Czochralski method or Czochralski method) and FZ (floating zone) -- although law, a smoke method, etc. are mentioned, it is not limited to these.

[0017] About the concentration of the intermingled impurity, it is usually the silicon atom 107. An individual to 106 Although it is the rate of a donor atom or one acceptor atom, desirable high-concentration doping is suitable for the individual, and it is the silicon atom 104. It is desirable to an individual that they are the rate of a donor atom or one acceptor atom or the high concentration beyond it. It is 20 degrees C, more than 10^{-5} Scm⁻¹ is more than 10^{-2} Scm⁻¹ desirable still more preferably, and the electrical conductivity sigma obtained by doping such an impurity etc. is more than 1 Scm⁻¹ most preferably.

[0018] The covalent crystal used for this invention has the desirable fine particles which are the average grain size of 0.1-500 micrometers. A grinder and a classifier are used in order to obtain the fine particles of a predetermined configuration. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a planet ball mill, a jet mill, a counter jet mill, a turning air-current mold jet mill, a screen, etc. are used. At the time of grinding, wet grinding which made organic solvents, such as water or a hexane, live together can also be used. As the classification approach, there is especially no definition and a screen, a pneumatic elutriation machine, etc. are used if needed in dry type and wet.

[0019] The organic compound which contains lithiums, such as a lithium metal, a lithium alloy, etc. a baking carbonaceous compound that can carry out occlusion bleedoff of a lithium ion or the lithium metal, a chalcogen compound, and methyl lithium, as a negative-electrode ingredient which can be combined and can be used for this invention is mentioned. Moreover, it is also possible by using together the organic compound containing a lithium metal, a lithium alloy, and a lithium to insert a lithium in the alloy of the covalent crystal used for this invention and a lithium inside a cell further.

[0020] the case where the covalent crystal of this invention and the alloy of a lithium are used as powder -- an electrode -- an electric conduction agent, a binder, a filler, etc. can be added as a mixture. If it is the electronic conduction nature ingredient which does not have an adverse effect on the cell engine performance as an electric conduction agent, it is good anything. Usually, conductive ingredients, such as vacuum evaporation of natural graphites (flaky graphite, a scale-like graphite, earthy graphite, etc.), an artificial graphite, carbon black, acetylene black, KETCHIEN black, a carbon whisker, carbon fiber metallurgy group powder (copper, nickel, aluminum, silver, gold, etc.), a metal fiber, and a metal and a conductive ceramic ingredient, can be included as one sort or those mixture. In these, concomitant use of a graphite, acetylene black, and KETCHIEN black is desirable. The addition has 1 - 50 desirable % of the weight, and its 2 - 30 % of the weight is especially desirable.

[0021] As a binder, a polymer, polysaccharide, etc. which have thermoplastics, such as tetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), sulfonation EPDM, styrene butadiene rubber (SBR), a fluororubber, and

a KARUBO methoxy cellulose, and rubber elasticity can usually be used as one sort or two sorts or more of mixture. Moreover, as for a lithium and the binder which has the functional group which reacts, it is desirable like polysaccharide to methylate, for example and to carry out deactivation of the functional group. As the addition, 1 - 50 % of the weight is desirable, and 2 - 30 % of the weight is especially desirable.

[0022] If it is the ingredient which does not have an adverse effect on the cell engine performance as a filler, it is good anything. Usually, olefin system polymers, such as polypropylene and polyethylene, Aerosil, a zeolite, glass, carbon, etc. are used. The addition of a filler has 0 - 30 desirable % of the weight.

[0023] If it is the electronic conductor which does not do an adverse effect in the constituted cell as a charge collector of an electrode active material, it is good anything. For example, as an ingredient of a positive-electrode charge collector, besides aluminum, titanium, stainless steel, nickel, baking carbon, a conductive polymer, electrically conductive glass, etc., it is the object of an adhesive property, conductivity, and oxidation-resistant improvement, and what processed front faces, such as aluminum and copper, with carbon, nickel, titanium, silver, etc. can be used. As an ingredient of a negative-electrode charge collector, besides copper, stainless steel, nickel, aluminum, titanium, baking carbon, a conductive polymer, electrically conductive glass, an aluminum-Cd alloy, etc., it is the object of an adhesive property, conductivity, and oxidation-resistant improvement, and what processed front faces, such as copper, with carbon, nickel, titanium, silver, etc. can be used. About these ingredients, it is also possible to oxidize a front face. About these configurations, the shape of the shape of the shape of others and a film and a sheet and a network, punch or the configuration by which expanded one was carried out, a lath object, a porous body, a firing object, the organizer of a fiber group, etc. are used. [shape / of foil] Although especially definition is thin, a 1-500-micrometer thing is used.

[0024] Thus, the alloy of the covalent crystal obtained and a lithium can be used as a negative-electrode active material. on the other hand -- as positive active material -- MnO_2 , MoO_3 , V_2O_5 , Li_xCoO_2 , Li_xNiO_2 , and $\text{Li}_x\text{Mn}_2\text{O}_4$ etc. -- a metallic oxide, and TiS_2 , MoS_2 and NbSe_3 etc. -- various kinds of matter in which absorption/emission is possible can be used for alkali-metal ion, such as intercalated graphite, such as a metal chalcogen ghost, the poly acene, poly para-phenylene, polypyrrole, and the poly aniline, and a conductive polymer, and an anion.

[0025] When the covalent crystal of this invention and the alloy of a lithium are especially used as a negative-electrode active material, The viewpoint of a high energy consistency to V_2O_5 , MnO_2 , Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, $\text{Li}_x\text{Fe}_2\text{O}_3(\text{SO}_4)$, Li_xFePO_4 , and $\text{Li}_{1+x}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Li}_{3+x}\text{Fe}_2\text{O}_3(\text{PO}_4)$ etc. -- what has the electrode potential of 2-4V is desirable. especially -- Li_xCoO_2 , Li_xNiO_2 , and $\text{Li}_x\text{Mn}_2\text{O}_4$ etc. -- a lithium content transition-metals oxide is desirable.

[0026] Moreover, it is desirable to be able to use the organic electrolytic solution, a solid polymer electrolyte, an inorganic solid electrolyte, fused salt, etc., for example, and to use the organic electrolytic solution also in this as an electrolyte. As an organic solvent of this organic electrolytic solution, propylene carbonate, ethylene carbonate, Butylene carbonate, diethyl carbonate, dimethyl carbonate, Ester, such as methylethyl carbonate and gamma-butyrolactone Permutation tetrahydrofurans, such as a tetrahydrofuran and 2-methyl tetrahydrofuran, Dioxolane, diethylether, dimethoxyethane, diethoxy ethane, Ether, such as methoxyethoxy ethane, dimethyl sulfoxide, a sulfolane, a methyl sulfolane, an acetonitrile, methyl formate, methyl acetate, N-methyl pyrrolidone, dimethyl formamide, etc. are mentioned, and these can be used as independent or a mixed solvent. moreover -- as a supporting-electrolyte salt -- LiClO_4 , LiPF_6 , LiBF_4 , LiAsF_6 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ etc. -- it is mentioned. On the other hand, what melted the above supporting-electrolyte salts as a giant-molecule solid electrolyte into polymers, such as polyethylene oxide, the bridge formation object and poly FOSUFAZEN, and its bridge formation object, can be used. Furthermore, inorganic solid electrolytes, such as Li_3N and LiI , are also usable. That is, what is necessary is just

nonaqueous electrolyte of lithium ion conductivity.

[0027] As a separator, the transmittance of ion is excellent and an insulating thin film with a mechanical strength can be used. The sheet built from organic solvent-proof nature and hydrophobicity from the polymer of olefin systems, such as polypropylene and polyethylene, a glass fiber, polyvinylidene fluoride, polytetrafluoroethylene, etc., a micropore film, and a nonwoven fabric are used. The aperture of a separator is a thing of the range generally used for a cell, for example, is 0.01-10 micrometers. Moreover, the same is said of the thickness, and it is the thing of the range generally used for a cell, for example, is 5-300 micrometers.

[0028] When using the covalent crystal of this invention as fine particles, the thing of the fine particles for which a surface-layer part is embellished at least is also possible. For example, applying techniques, such as plating, sintering, a mechano fusion, and vacuum evaporation, and carrying out the coat of the ion conductivity good matter, such as good matter of electronic conduction nature, such as gold, silver, carbon, nickel, and copper, and a lithium carbonate, boron glass, a solid electrolyte, is mentioned.

[0029] As a reason such an outstanding charge-and-discharge property is acquired, although it is not necessarily clear, it is considered as follows. That is, it can observe that an alloy with a lithium is possible for the crystal which has covalent bond, and the abundance ratio of the lithium in the alloy is large. However, although the crystal which has covalent bond is a semi-conductor, it is an intrinsic semiconductor, and the electrical conductivity in the ordinary temperature has polarization comparatively large [a crystal] at the time of charge and discharge low. On the other hand, the lithium alloy by which occlusion was carried out by carrying out occlusion as a lithium alloy by electronic conduction nature's improving if the impurity which can serve as a donor atom and an acceptor atom into a covalent crystal is doped, and polarization at the time of charge and discharge becoming small, and giving an electron easily to a lithium ion emits an electron easily, and it is emitted as a lithium ion. That is, by acquiring the mechanism in which a covalent crystal pours an electron, the electron flow inside a crystal becomes smooth and it is presumed that occlusion bleedoff of a lithium ion is made easy. Moreover, since the crystal structure of silicon or a gallium is the same face centered cubic structure as a diamond, association of a crystal is dramatically firm and it follows in footsteps of dilatation contraction in connection with occlusion bleedoff of a lithium, and an active material's own detailed-izing or omission are not seen, but it is considered to raise the reversibility of charge and discharge. Furthermore, if a single crystal is used, since a grain boundary does not exist in the interior of a crystal, even if dilatation contraction of a crystal arises at the time of occlusion bleedoff of a lithium, a grain boundary is not covered with stress, as a result, neither own pulverization of an active material nor omission is seen, but it is considered that the reversibility of charge and discharge is improving.

[0030] The negative-electrode active material which makes the covalent crystal of this invention the quality of a main truss product can carry out occlusion bleedoff of the lithium ion in 0-2V at least to a metal lithium into nonaqueous electrolyte. Moreover, the fine pulverization at the time of the charge and discharge looked at by the usual alloy and partial electric isolation of a negative-electrode active material are suppressed from a covalent crystal being firm. Moreover, if the impurity which can become a covalent crystal with a donor atom and an acceptor atom beforehand is doped, electronic conduction nature will improve and alloying of a covalent crystal and a lithium will be made smooth. Moreover, by dealing with such a covalent crystal as powdered, it becomes possible to coat on a charge collector, and the design of the various cell configurations of the shape of a cylinder, a square shape, flatness, coin, and a film is attained. Moreover, using together with an electric conduction agent also becomes possible, and the rate property's of charge and discharge improves. Furthermore, since negative-electrode potential is close to lithium potential and low, the electrical potential difference as a cell turns into high tension, and since the amount which can carry out occlusion of the lithium is large, moreover, a high energy consistency is attained. If a single

crystal is used especially as a covalent crystal, since a grain boundary does not exist in the interior of a crystal, even if dilatation contraction of a crystal arises at the time of occlusion bleedoff of a lithium, a grain boundary is not covered with stress, as a result, an active material's own detailed-izing or omission will not be seen, but it will be considered to raise the reversibility of charge and discharge. The own toxicity of silicon of moreover using silicon as a negative-electrode ingredient is low, and especially since it is ingredients abundant in resource, it is excellent. By using such a negative-electrode active material as an electrode material, by high tension and the high energy consistency, the outstanding charge-and-discharge cycle property can be shown, and a nonaqueous electrolyte cell with high safety can be obtained.

[0031]

[Embodiment of the Invention] Hereafter, the example of this invention is explained.

(Example 1) By the diffusion method, it is the silicon atom 104. The silicon single crystal which is the n-type semiconductor doped at a rate of one P atom to the individual (a), Silicon atom 104 The silicon polycrystal which is the n-type semiconductor doped at a rate of one P atom to the individual (b), Silicon atom 104 They are (c) and the silicon atom 104 about the silicon single crystal which is the p type semiconductor doped at a rate of one B atom to the individual. Silicon polycrystal which is the p type semiconductor doped at a rate of one B atom to the individual is set to (d). This specific resistance was 20 degrees C, the n-type semiconductor was 33Scm-1 and the p type semiconductor was 20Scm-1. The mortar ground each covalent-bond nature crystal, and the coin mold lithium secondary battery was made as an experiment as follows using these negative-electrode active materials. A negative-electrode active material, acetylene black, and polytetrafluoroethylene powder were mixed by the weight ratio 85:10:5, toluene was added, and it kneaded enough. This was fabricated with a thickness of 0.3mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, it heat-treated at 200 degrees C under reduced pressure for 15 hours, and the negative electrode 2 was obtained. The negative electrode 2 was stuck by pressure and used for the negative-electrode can 5 to which the negative-electrode charge collector 7 was attached.

[0032] A positive electrode 1 is LiCoO₂ as positive active material. Acetylene black and polytetrafluoroethylene powder were mixed by the weight ratio 85:10:5, and what added toluene and was kneaded enough was used. This was fabricated with a thickness of 0.8mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, it heat-treated at 200 degrees C under reduced pressure for 15 hours, and the positive electrode 1 was obtained. The positive electrode 1 was stuck by pressure and used for the positive-electrode can 4 to which the positive-electrode charge collector 6 was attached. It is LiPF₆ to the partially aromatic solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate. The fine porous membrane made from polypropylene was used for the separator 3 using the electrolytic solution which dissolved in the concentration of one mol/l. The coin mold lithium cell with a diameter [of 20mm] and a thickness of 1.6mm was produced using the above-mentioned positive electrode, a negative electrode, the electrolytic solution, and a separator. These covalent-bond nature crystal (a) The cell using - (d) is made into (A) - (D), respectively.

[0033] (Example 1 of a comparison) The single crystal (e) of a gallium arsenide was used as a covalent-bond nature crystal which does not contain an impurity. This specific resistance was 10-8Scm-1 at 20 degrees C. The coin mold lithium cell was produced like the above-mentioned example 1 except this. The obtained cell is set to (E).

[0034] (Example 2 of a comparison) The aluminium powder was used instead of the covalent-bond nature crystal, and the coin mold lithium cell was produced like the above-mentioned example 1 except it. The obtained cell is set to (F). Thus, the capacity test of the produced coin mold lithium cell was performed. Although occlusion bleedoff of a lithium was checked about (A) - (E) using a covalent-bond nature crystal, and (F) using a metallic crystal, about the cel (D) using a covalent

crystal lower than 10^{-5} Scm⁻¹, bleedoff of a lithium was hardly completed at 20 degrees C. The capacity of the first stage at this time and the capacity of 10 cycle eye were shown in a table 1. About the cel (E) using the covalent crystal lower than 10^{-5} Scm⁻¹ at 20 degrees C, resistance is strong, and it can observe that occlusion bleedoff of the lithium to silicon could not take place easily. Moreover, about (F) using a metallic crystal, it can observe that it is lacking in the reversibility of charge and discharge so that clearly from this result. It is thought that it will be for the active materials electrically isolated by the pulverization produced in the case of alloying of a metallic crystal and a lithium to increase in number. About the negative electrode using the covalent-bond nature crystal whose electronic conduction nature doped the impurity which is this invention and improved, it excels in charge-and-discharge cycle nature, and it turns out that it is high capacity. In covalent-bond nature crystal (A) - (D) whose electronic conduction nature doped the still more nearly same impurity and improved, it can observe that the cycle property is improving from (B) using polycrystal, and (D) in (A) using a single crystal, and (C). That is, it is thought that a single crystal is because own pulverization of an active material and omission controlled, and its cycle property improved as the result, without covering a grain boundary with stress even if expansion of a crystal and contraction arose at the time of the occlusion of a lithium and bleedoff since a grain boundary does not exist in the interior of a crystal.

[0035]

[A table 1]

電池	1 サイクル(mAh)		10 サイクル(mAh)	
	充電容量	放電容量	充電容量	放電容量
A	65	63	62	62
B	64	62	60	59
C	63	61	62	62
D	63	62	59	58
E	60	1	0	0
F	65	62	30	28

[0036] In the example, although electrical conductivity sigma mentioned silicon as a covalent crystal beyond 10^{-5} Scm⁻¹ at 20 degrees C, the same effectiveness was checked about other covalent crystals. In addition, this invention is not limited to the start raw material, the manufacture approach, a positive electrode, a negative electrode, an electrolyte, a separator, a cell configuration, etc. of the active material indicated by the above-mentioned example.

[0037]

[Effect of the Invention] Since this invention is constituted like ****, it is high tension, high capacity, and a high energy consistency, and the outstanding charge-and-discharge cycle property is shown, and a nonaqueous electrolyte cell with high safety can be offered.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the negative-electrode active material in more detail about a nonaqueous electrolyte cell.

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PRIOR ART

[Description of the Prior Art] Although it was more typical than before as a negative-electrode active material for nonaqueous electrolyte cells to have used a lithium, there was a problem in respect of a cycle life for an arborescence deposit (dendrite) of the lithium generated at the time of charge. Moreover, this dendrite penetrates a separator, and an internal short circuit is caused or it causes ignition.

[0003] Moreover, the alloy with a metal lithium was also used in order to prevent the dendrite generated at the time of the above charge, but when the charge became large, there were problems, such as fine pulverization of a negative electrode and omission of a negative-electrode active material.

[0004] The cell which uses a carbon material for a negative electrode for current, reinforcement, and safety attracts attention, and is put in practical use in part. However, the carbon material used for a negative electrode had the problem that an internal short circuit and decline in charging efficiency arose, at the time of boosting charge. Generally, since the dope potential of the lithium to a carbon material was close to 0V, potential might become less than [0V] and these carbon materials might deposit the lithium on the electrode, when boosting charge was performed. Therefore, the internal short circuit of a cell is caused or it becomes the cause that discharge effectiveness falls. Moreover, although the improvement with such a carbon material remarkable in respect of a cycle life is made, since the consistency is comparatively small, the capacity per volume will become low. That is, this carbon material is still insufficient from the point of a high energy consistency. Moreover, initial charge-and-discharge effectiveness falls about what needs to form a coat on carbon, and since quantity of electricity used for this coat formation is irreversible, it leads to the capacity lowering for that quantity of electricity.

[0005] On the other hand, multiple oxide $\text{Li}_x \text{Si}_{1-y} \text{M}_y \text{O}_z$ (JP,7-230800,A) containing silicon and a lithium and using amorphous chalcogen compound $\text{M}_1 \text{M}_2 \text{p M}_4 \text{q}$ (JP,7-288123,A) are advocated as negative-electrode active materials other than a metal lithium, a lithium alloy, or a carbon material, and it is improved in respect of high capacity and a high energy consistency.

[0006] However, since the own electrical conductivity of an active material of the above multiple oxides was low, the problem was in boosting charge and a load characteristic. Although addition of an electric conduction agent is tried in order to solve this problem, in order to acquire the charge-and-discharge property that satisfaction is obtained, it is necessary to use amount sufficient as an electric conduction agent for a carbon material with a low consistency, and the capacity per volume will fall.

[0007] Moreover, since a multiple oxide etc. was considered that a reaction with a lithium advances through reduction of oxide since the ingredient itself is oxide, especially the irreversible reduction in the first stage might take place, and initial charge-and-discharge effectiveness might become low. Therefore, by the further high capacity and the high energy consistency, a cycle life is long and development of the safe negative-electrode ingredient for nonaqueous electrolyte cells is desired.

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EFFECT OF THE INVENTION

[Effect of the Invention] Since this invention is constituted like ****, it is high tension, high capacity, and a high energy consistency, and the outstanding charge-and-discharge cycle property is shown, and a nonaqueous electrolyte cell with high safety can be offered.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] That is, although it is advantageous in respect of high tension and safety when a problem has an advantage as high tension, and high capacity and a high energy consistency on the cycle nature of a certain thing, or safety when using the alloy of a lithium metal, or a lithium and a metal as a negative electrode, and using a carbon material, the field of high capacity and a high energy consistency is inadequate. Furthermore, when using an oxide negative electrode, the point of high capacity and a high energy consistency is not satisfactory in respect of high tension, a charge-and-discharge effectiveness property, and a cycle life or safety, although it seems that it is improved.

[0009] For this reason, in order to show the outstanding charge-and-discharge cycle property and to obtain a rechargeable battery with high safety by high tension and the high energy consistency, there are few change and the volume changes of crystal system in the case of occlusion bleedoff of the lithium at the time of charge and discharge, and it is expected the compound which is an operating space near lithium potential as much as possible, and has reversibly the conductivity which can occlusion emit a lithium.

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MEANS

[Means for Solving the Problem] This invention is made in view of the above-mentioned trouble, and it is characterized by electrical conductivity σ consisting [the quality of a main truss product of a negative-electrode active material] of a covalent crystal beyond 10^{-5}Scm^{-1} at 20 degrees C as an ideal negative-electrode active material used for a nonaqueous electrolyte cell. [0011] Furthermore, as for the quality of a main truss product of the negative-electrode active material mentioned above, consisting of a powder-like silicon single crystal is desirable. [0012] previously -- as the alloy of a lithium and silicon -- Binary Alloy Phase it is in Diagrams (p2465) -- as -- $\text{Li}_{22}\text{Si}_5$ up to -- alloying by presentation is known. Moreover, JP,5-74463,A has reported that a cycle property improves by using the single crystal of silicon for a negative electrode. However, when silicon was made to dope a lithium as negative-electrode material of the nonaqueous electrolyte cell for rapid charges and discharges and having been tried as like, it turned out that a lithium deposits without a dope hardly taking place. Then, as a result of this invention persons' performing examination on an electronic conduction disposition about a covalent crystal, it turned out that the occlusion of a lithium and bleedoff advance smoothly, without the phenomenon of a deposit of a lithium happening. Furthermore, it turned out that this reaction advances with the potential very near lithium potential about 0.1V, the high capacity near geometric capacity is obtained, and it excels in reversibility.

[0013] That is, although the alloy of a lithium and silicon was known, it was the intrinsic semiconductor of a covalent crystal originally, if silicon itself remained as it was, its electronic conduction nature was low, and the property as a cell negative-electrode ingredient was bad [itself]. Therefore, although it was the raw material which cannot be easily set as the object of research, it found out that electronic conduction nature improved and occlusion bleedoff of a lithium took place easily by doping the atom which can become silicon with a donor atom and an acceptor atom as an ingredient built into the interior of a cell. It turned out that phenomena, such as breaking or impalpable-powder-izing of a crystal, or omission, are not seen by using silicon as a single crystal especially, but a cycle property improves.

[0014]

[Embodiment of the Invention] Although the charge-and-discharge property which Si, germanium, GaAs, GaP, InSb, GaP, SiC, BN, etc. were mentioned, among those was excellent about especially silicon as a covalent crystal said here is acquired, and it is abundant in resource, and it is desirable especially since toxicity is low, it is not limited to these. Moreover, although it is desirable since the charge-and-discharge property which a single crystal, polycrystal, and amorphous ** were mentioned about the crystal system, among those was excellent about especially the single crystal is acquired, it is not limited to these.

[0015] Furthermore, this covalent crystal can contain an impurity in order to raise electronic conduction nature. Although the impurity said here can serve as a donor atom and an acceptor atom among all the elements of the periodic table and are P, aluminum, As, Sb, B, Ga, In, etc. preferably,

it is not limited to these.

[0016] as the approach of obtaining the single crystal of silicon -- a CZ process (Czochralski method or Czochralski method) and FZ (floating zone) -- although law, a smoke method, etc. are mentioned, it is not limited to these.

[0017] About the concentration of the intermingled impurity, it is usually the silicon atom 107. An individual to 106 Although it is the rate of a donor atom or one acceptor atom, desirable high-concentration doping is suitable for the individual, and it is the silicon atom 104. It is desirable to an individual that they are the rate of a donor atom or one acceptor atom or the high concentration beyond it. It is 20 degrees C, more than 10^{-5} Scm⁻¹ is more than 10^{-2} Scm⁻¹ desirable still more preferably, and the electrical conductivity sigma obtained by doping such an impurity etc. is more than 1 Scm⁻¹ most preferably.

[0018] The covalent crystal used for this invention has the desirable fine particles which are the average grain size of 0.1-500 micrometers. A grinder and a classifier are used in order to obtain the fine particles of a predetermined configuration. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a planet ball mill, a jet mill, a counter jet mill, a turning air-current mold jet mill, a screen, etc. are used. At the time of grinding, wet grinding which made organic solvents, such as water or a hexane, live together can also be used. As the classification approach, there is especially no definition and a screen, a pneumatic elutriation machine, etc. are used if needed in dry type and wet.

[0019] The organic compound which contains lithiums, such as a lithium metal, a lithium alloy, etc. a baking carbonaceous compound that can carry out occlusion bleedoff of a lithium ion or the lithium metal, a chalcogen compound, and methyl lithium, as a negative-electrode ingredient which can be combined and can be used for this invention is mentioned. Moreover, it is also possible by using together the organic compound containing a lithium metal, a lithium alloy, and a lithium to insert a lithium in the alloy of the covalent crystal used for this invention and a lithium inside a cell further.

[0020] the case where the covalent crystal of this invention and the alloy of a lithium are used as powder -- an electrode -- an electric conduction agent, a binder, a filler, etc. can be added as a mixture. If it is the electronic conduction nature ingredient which does not have an adverse effect on the cell engine performance as an electric conduction agent, it is good anything. Usually, conductive ingredients, such as vacuum evaporation of natural graphites (flaky graphite, a scale-like graphite, earthy graphite, etc.), an artificial graphite, carbon black, acetylene black, KETCHIEN black, a carbon whisker, carbon fiber metallurgy group powder (copper, nickel, aluminum, silver, gold, etc.), a metal fiber, and a metal and a conductive ceramic ingredient, can be included as one sort or those mixture. In these, concomitant use of a graphite, acetylene black, and KETCHIEN black is desirable. The addition has 1 - 50 desirable % of the weight, and its 2 - 30 % of the weight is especially desirable.

[0021] As a binder, a polymer, polysaccharide, etc. which have thermoplastics, such as tetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), sulfonation EPDM, styrene butadiene rubber (SBR), a fluororubber, and a KARUBO methoxy cellulose, and rubber elasticity can usually be used as one sort or two sorts or more of mixture. Moreover, as for a lithium and the binder which has the functional group which reacts, it is desirable like polysaccharide to methylate, for example and to carry out deactivation of the functional group. As the addition, 1 - 50 % of the weight is desirable, and 2 - 30 % of the weight is especially desirable.

[0022] If it is the ingredient which does not have an adverse effect on the cell engine performance as a filler, it is good anything. Usually, olefin system polymers, such as polypropylene and polyethylene, Aerosil, a zeolite, glass, carbon, etc. are used. The addition of a filler has 0 - 30 desirable % of the weight.

[0023] If it is the electronic conductor which does not do an adverse effect in the constituted cell as a charge collector of an electrode active material, it is good anything. For example, as an ingredient of a positive-electrode charge collector, besides aluminum, titanium, stainless steel, nickel, baking carbon, a conductive polymer, electrically conductive glass, etc., it is the object of an adhesive property, conductivity, and oxidation-resistant improvement, and what processed front faces, such as aluminum and copper, with carbon, nickel, titanium, silver, etc. can be used. As an ingredient of a negative-electrode charge collector, besides copper, stainless steel, nickel, aluminum, titanium, baking carbon, a conductive polymer, electrically conductive glass, an aluminum-Cd alloy, etc., it is the object of an adhesive property, conductivity, and oxidation-resistant improvement, and what processed front faces, such as copper, with carbon, nickel, titanium, silver, etc. can be used. About these ingredients, it is also possible to oxidize a front face. About these configurations, the shape of the shape of the shape of others and a film and a sheet and a network, punch or the configuration by which expanded one was carried out, a lath object, a porous body, a firing object, the organizer of a fiber group, etc. are used. [shape / of foil] Although especially definition is thin, a 1-500-micrometer thing is used.

[0024] Thus, the alloy of the covalent crystal obtained and a lithium can be used as a negative-electrode active material. on the other hand -- as positive active material -- MnO_2 , MoO_3 , V_2O_5 , Li_xCoO_2 , Li_xNiO_2 , and $\text{Li}_x\text{Mn}_2\text{O}_4$ etc. -- a metallic oxide, and TiS_2 , MoS_2 and NbSe_3 etc. -- various kinds of matter in which absorption/emission is possible can be used for alkali-metal ion, such as intercalated graphite, such as a metal chalcogen ghost, the poly acene, poly para-phenylene, polypyrrole, and the poly aniline, and a conductive polymer, and an anion.

[0025] When the covalent crystal of this invention and the alloy of a lithium are especially used as a negative-electrode active material, The viewpoint of a high energy consistency to V_2O_5 , MnO_2 , Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, $\text{Li}_x\text{Fe}_2\text{O}_3(\text{SO}_4)$, Li_xFePO_4 , and $\text{Li}_{1+x}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Li}_{3+x}\text{Fe}_2\text{O}_3(\text{PO}_4)$ etc. -- what has the electrode potential of 2-4V is desirable. especially -- Li_xCoO_2 , Li_xNiO_2 , and $\text{Li}_x\text{Mn}_2\text{O}_4$ etc. -- a lithium content transition-metals oxide is desirable.

[0026] Moreover, it is desirable to be able to use the organic electrolytic solution, a solid polymer electrolyte, an inorganic solid electrolyte, fused salt, etc., for example, and to use the organic electrolytic solution also in this as an electrolyte. As an organic solvent of this organic electrolytic solution, propylene carbonate, ethylene carbonate, Butylene carbonate, diethyl carbonate, dimethyl carbonate, Ester, such as methylethyl carbonate and gamma-butyrolactone Permutation tetrahydrofurans, such as a tetrahydrofuran and 2-methyl tetrahydrofuran, Dioxolane, diethylether, dimethoxyethane, diethoxy ethane, Ether, such as methoxyethoxy ethane, dimethyl sulfoxide, a sulfolane, a methyl sulfolane, an acetonitrile, methyl formate, methyl acetate, N-methyl pyrrolidone, dimethyl formamide, etc. are mentioned, and these can be used as independent or a mixed solvent. moreover -- as a supporting-electrolyte salt -- LiClO_4 , LiPF_6 , LiBF_4 , LiAsF_6 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ etc. -- it is mentioned. On the other hand, what melted the above supporting-electrolyte salts as a giant-molecule solid electrolyte into polymers, such as polyethylene oxide, the bridge formation object and poly FOSUFAZEN, and its bridge formation object, can be used. Furthermore, inorganic solid electrolytes, such as Li_3N and LiI , are also usable. That is, what is necessary is just nonaqueous electrolyte of lithium ion conductivity.

[0027] As a separator, the transmittance of ion is excellent and an insulating thin film with a mechanical strength can be used. The sheet built from organic solvent-proof nature and hydrophobicity from the polymer of olefin systems, such as polypropylene and polyethylene, a glass fiber, polyvinylidene fluoride, polytetrafluoroethylene, etc., a micropore film, and a nonwoven fabric are used. The aperture of a separator is a thing of the range generally used for a cell, for example, is 0.01-10 micrometers. Moreover, the same is said of the thickness, and it is the thing of the range generally used for a cell, for example, is 5-300 micrometers.

[0028] When using the covalent crystal of this invention as fine particles, the thing of the fine

particles for which a surface-layer part is embellished at least is also possible. For example, applying techniques, such as plating, sintering, a mechano fusion, and vacuum evaporation, and carrying out the coat of the ion conductivity good matter, such as good matter of electronic conduction nature, such as gold, silver, carbon, nickel, and copper, and a lithium carbonate, boron glass, a solid electrolyte, is mentioned.

[0029] As a reason such an outstanding charge-and-discharge property is acquired, although it is not necessarily clear, it is considered as follows. That is, it can observe that an alloy with a lithium is possible for the crystal which has covalent bond, and the abundance ratio of the lithium in the alloy is large. However, although the crystal which has covalent bond is a semi-conductor, it is an intrinsic semiconductor, and the electrical conductivity in the ordinary temperature has polarization comparatively large [a crystal] at the time of charge and discharge low. On the other hand, the lithium alloy by which occlusion was carried out by carrying out occlusion as a lithium alloy by electronic conduction nature's improving if the impurity which can serve as a donor atom and an acceptor atom into a covalent crystal is doped, and polarization at the time of charge and discharge becoming small, and giving an electron easily to a lithium ion emits an electron easily, and it is emitted as a lithium ion. That is, by acquiring the mechanism in which a covalent crystal pours an electron, the electron flow inside a crystal becomes smooth and it is presumed that occlusion bleedoff of a lithium ion is made easy. Moreover, since the crystal structure of silicon or a gallium is the same face centered cubic structure as a diamond, association of a crystal is dramatically firm and it follows in footsteps of dilatation contraction in connection with occlusion bleedoff of a lithium, and an active material's own detailed-izing or omission are not seen, but it is considered to raise the reversibility of charge and discharge. Furthermore, if a single crystal is used, since a grain boundary does not exist in the interior of a crystal, even if dilatation contraction of a crystal arises at the time of occlusion bleedoff of a lithium, a grain boundary is not covered with stress, as a result, neither own pulverization of an active material nor omission is seen, but it is considered that the reversibility of charge and discharge is improving.

[0030] The negative-electrode active material which makes the covalent crystal of this invention the quality of a main truss product can carry out occlusion bleedoff of the lithium ion in 0-2V at least to a metal lithium into nonaqueous electrolyte. Moreover, the fine pulverization at the time of the charge and discharge looked at by the usual alloy and partial electric isolation of a negative-electrode active material are suppressed from a covalent crystal being firm. Moreover, if the impurity which can become a covalent crystal with a donor atom and an acceptor atom beforehand is doped, electronic conduction nature will improve and alloying of a covalent crystal and a lithium will be made smooth. Moreover, by dealing with such a covalent crystal as powdered, it becomes possible to coat on a charge collector, and the design of the various cell configurations of the shape of a cylinder, a square shape, flatness, coin, and a film is attained. Moreover, using together with an electric conduction agent also becomes possible, and the rate property's of charge and discharge improves. Furthermore, since negative-electrode potential is close to lithium potential and low, the electrical potential difference as a cell turns into high tension, and since the amount which can carry out occlusion of the lithium is large, moreover, a high energy consistency is attained. If a single crystal is used especially as a covalent crystal, since a grain boundary does not exist in the interior of a crystal, even if dilatation contraction of a crystal arises at the time of occlusion bleedoff of a lithium, a grain boundary is not covered with stress, as a result, an active material's own detailed-izing or omission will not be seen, but it will be considered to raise the reversibility of charge and discharge. The own toxicity of silicon of moreover using silicon as a negative-electrode ingredient is low, and especially since it is ingredients abundant in resource, it is excellent. By using such a negative-electrode active material as an electrode material, by high tension and the high energy consistency, the outstanding charge-and-discharge cycle property can be shown, and a nonaqueous electrolyte cell with high safety can be obtained.

[0031]

[Embodiment of the Invention] Hereafter, the example of this invention is explained.

(Example 1) By the diffusion method, it is the silicon atom 104. The silicon single crystal which is the n-type semiconductor doped at a rate of one P atom to the individual (a), Silicon atom 104 The silicon polycrystal which is the n-type semiconductor doped at a rate of one P atom to the individual (b), Silicon atom 104 They are (c) and the silicon atom 104 about the silicon single crystal which is the p type semiconductor doped at a rate of one B atom to the individual. Silicon polycrystal which is the p type semiconductor doped at a rate of one B atom to the individual is set to (d). This specific resistance was 20 degrees C, the n-type semiconductor was 33Scm^{-1} and the p type semiconductor was 20Scm^{-1} . The mortar ground each covalent-bond nature crystal, and the coin mold lithium secondary battery was made as an experiment as follows using these negative-electrode active materials. A negative-electrode active material, acetylene black, and polytetrafluoroethylene powder were mixed by the weight ratio 85:10:5, toluene was added, and it kneaded enough. This was fabricated with a thickness of 0.3mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, it heat-treated at 200 degrees C under reduced pressure for 15 hours, and the negative electrode 2 was obtained. The negative electrode 2 was stuck by pressure and used for the negative-electrode can 5 to which the negative-electrode charge collector 7 was attached.

[0032] A positive electrode 1 is LiCoO_2 as positive active material. Acetylene black and polytetrafluoroethylene powder were mixed by the weight ratio 85:10:5, and what added toluene and was kneaded enough was used. This was fabricated with a thickness of 0.8mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, it heat-treated at 200 degrees C under reduced pressure for 15 hours, and the positive electrode 1 was obtained. The positive electrode 1 was stuck by pressure and used for the positive-electrode can 4 to which the positive-electrode charge collector 6 was attached. It is LiPF_6 to the partially aromatic solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate. The fine porous membrane made from polypropylene was used for the separator 3 using the electrolytic solution which dissolved in the concentration of one mol/l. The coin mold lithium cell with a diameter [of 20mm] and a thickness of 1.6mm was produced using the above-mentioned positive electrode, a negative electrode, the electrolytic solution, and a separator. These covalent-bond nature crystal (a) The cell using - (d) is made into (A) - (D), respectively.

[0033] (Example 1 of a comparison) The single crystal (e) of a gallium arsenide was used as a covalent-bond nature crystal which does not contain an impurity. This specific resistance was $10\text{--}8\text{Scm}^{-1}$ at 20 degrees C. The coin mold lithium cell was produced like the above-mentioned example 1 except this. The obtained cell is set to (E).

[0034] (Example 2 of a comparison) The aluminium powder was used instead of the covalent-bond nature crystal, and the coin mold lithium cell was produced like the above-mentioned example 1 except it. The obtained cell is set to (F). Thus, the capacity test of the produced coin mold lithium cell was performed. Although occlusion bleedoff of a lithium was checked about (A) - (E) using a covalent-bond nature crystal, and (F) using a metallic crystal, about the cel (D) using a covalent crystal lower than $10\text{--}5\text{Scm}^{-1}$, bleedoff of a lithium was hardly completed at 20 degrees C. The capacity of the first stage at this time and the capacity of 10 cycle eye were shown in a table 1. About the cel (E) using the covalent crystal lower than $10\text{--}5\text{Scm}^{-1}$ at 20 degrees C, resistance is strong, and it can observe that occlusion bleedoff of the lithium to silicon could not take place easily. Moreover, about (F) using a metallic crystal, it can observe that it is lacking in the reversibility of charge and discharge so that clearly from this result. It is thought that it will be for the active materials electrically isolated by the pulverization produced in the case of alloying of a metallic crystal and a lithium to increase in number. About the negative electrode using the covalent-bond nature crystal whose electronic conduction nature doped the impurity which is this invention and

improved, it excels in charge-and-discharge cycle nature, and it turns out that it is high capacity. In covalent-bond nature crystal (A) - (D) whose electronic conduction nature doped the still more nearly same impurity and improved, it can observe that the cycle property is improving from (B) using polycrystal, and (D) in (A) using a single crystal, and (C). That is, it is thought that a single crystal is because own pulverization of an active material and omission controlled, and its cycle property improved as the result, without covering a grain boundary with stress even if expansion of a crystal and contraction arose at the time of the occlusion of a lithium and bleedoff since a grain boundary does not exist in the interior of a crystal.

[0035]

[A table 1]

電池	1 サイクル(mAh)		10 サイクル(mAh)	
	充電容量	放電容量	充電容量	放電容量
A	65	63	62	62
B	64	62	60	59
C	63	61	62	62
D	63	62	59	58
E	60	1	0	0
F	65	62	30	28

[0036] In the example, although electrical conductivity sigma mentioned silicon as a covalent crystal beyond 10^{-5}Scm^{-1} at 20 degrees C, the same effectiveness was checked about other covalent crystals. In addition, this invention is not limited to the start raw material, the manufacture approach, a positive electrode, a negative electrode, an electrolyte, a separator, a cell configuration, etc. of the active material indicated by the above-mentioned example.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the coin mold nonaqueous electrolyte cell concerning the example 2 of this invention.

[Description of Notations]

- 1 Negative Electrode
- 2 Positive Electrode
- 3 Separator
- 4 Negative-Electrode Can
- 5 Positive-Electrode Can
- 6 Negative-Electrode Charge Collector
- 7 Positive-Electrode Charge Collector
- 8 Insulating Packing

[Translation done.]

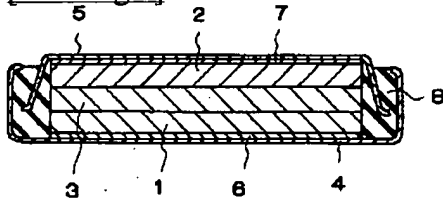
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DRAWINGS

[Drawing 1]



[Translation done.]

1. Amendment September 24, Heisei 16 (2004)

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CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law
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H01M 4/36
 H01M 4/02 D
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[Procedure amendment]
 [Filing Date] September 10, Heisei 15 (2003. 9.10)
 [Procedure amendment 1]
 [Document to be Amended] Description
 [Item(s) to be Amended] 0021
 [Method of Amendment] Modification
 [The content of amendment]
 [0021]

As a binder, a polymer, polysaccharide, etc. which have thermoplastics, such as tetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), sulfonation EPDM, styrene butadiene rubber (SBR), a fluororubber, and a carboxymethyl cellulose, and rubber elasticity can usually be used as one sort or two sorts or more of mixture. Moreover, as for a lithium and the binder which has the functional group which reacts, it is desirable like polysaccharide to methylate, for example and to carry out deactivation of the functional group. As the addition, 1 - 50 % of the weight is desirable, and 2 - 30 % of the weight is especially desirable.

[Translation done.]